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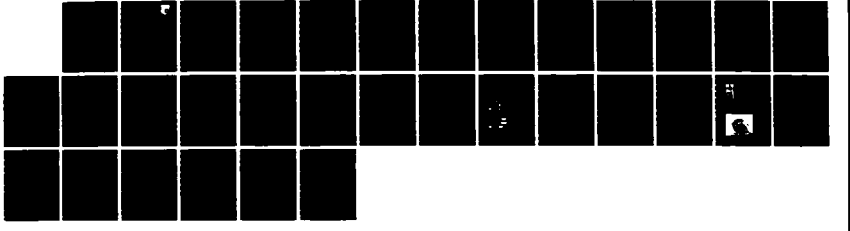

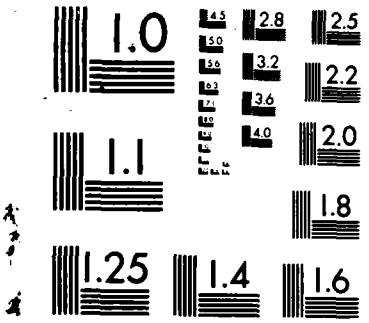

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EFFECTS OF CURE AND SIZING ON FIBER-MATRIX BOND STRENGTH

Piet W. M. Peters and George S. Springer
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Stanford University, Stanford, California

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Experiments were performed to evaluate the effects of cure and sizing on the bond strength between graphite fiber bundles and epoxy resins. Fiberite 976 and 934 resins and Thornel T300 (3K) fibers were used in the tests. The fibers were either uncoated (no sizing) or coated with different types of sizing. Pure resin specimens and resin specimens containing a single coated or uncoated fiber bundle were prepared by curing in a mold at different temperatures. The specimens were subjected to three point bending, and the load versus deflection curves were recorded. Photomicrographs of fiber bundles embedded in the resin were also taken. The data show the influence of the cure temperature (and the corresponding degree of cure) on the fracture strain and on the stiffness of the pure resins. The data also indicate the effects of cure temperature and sizing on the fiber bundle-resin bond strength (as manifested by the specimen's fracture strain), and the effect of sizing on the geometry of the bundle and on the fiber density inside the bundle.

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FOREWORD

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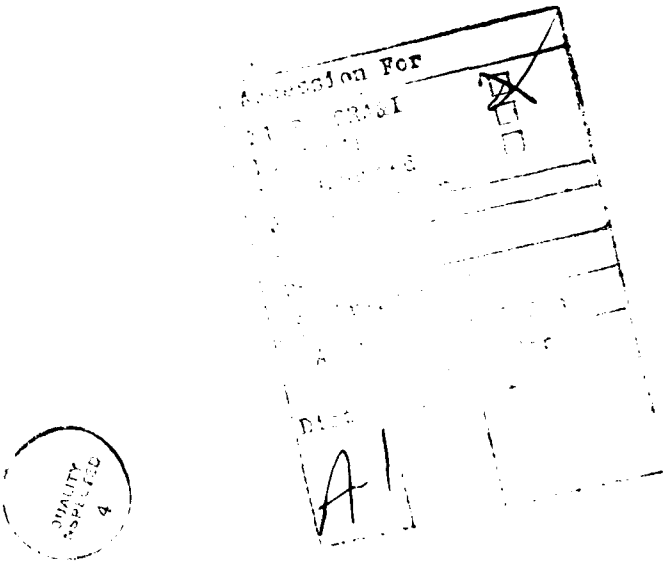

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Section I

INTRODUCTION

It is well recognized that the strength between the fibers and the matrix significantly affects the mechanical properties of fiber reinforced composites. For this reason, several investigators attempted to measure the bond strength between fibers and matrices [1–6]. Most of the previous studies were directed towards glass or Kevlar fibers embedded in epoxy resins [1–3]. Relatively little information is available on the bond strengths of graphite fibers in epoxy resin [4, 6]. The most comprehensive data for graphite fibers have been reported by Drzal et al. [4–5]. These investigators measured the bond strength of a single graphite fiber in a ductile resin.

There appears to be no data on the bond strengths of graphite fiber bundles in epoxy resins. Therefore, the objective of this investigation was to measure the bond strengths of graphite fiber bundles embedded in "brittle" resins. Fiber bundles (in contrast to single fibers) were selected for this study since such bundles are an essential part of composites made either by "prepreg" or by filament winding processes.

The bond strength may be affected by several factors, including cure, sizing, fiber surface treatment, and the morphology of the fiber surface. In this investigation attention was focused on the first two of these factors, namely on the effects of cure and sizing on the bond strength.

Section II

EXPERIMENTAL PROCEDURES

Commercially available resins and fibers were used in the tests. The resins were Fiberite 976 and Fiberite 934. These resins mainly consist of diaminodiphenyl sulfone (DDS) cured tetraglycidyl diaminodiphenyl methan (TGDDM) epoxy. Fiberite 934 also contains a second epoxy (diglycidyl orthophthalate) and BF_3 catalyst. These resins were selected for study because of the differences in their ductilities. Fiberite 976 and 934 have 2.3- and 1.0-percent fracture strains in tension, respectively [7]. The resins, received in "hot melt" form, were melted at 100°C and outgassed for one hour. The melted resin was then poured into the mold which was preheated to 100°C. A schematic of the mold is shown in Figure 1.

The 976 resin samples were cured at either 100°C (35 h 15 min), 140°C (5 h 27 min), 177°C (1 h 15 min), or 220°C (12 minutes). The 934 resin samples were cured at 95°C (22 h 40 min), 130°C (4 h 31 min), 170°C (1 h 23 min), and 210°C (25 minutes). In each case the initial heat-up rate was 3°C per minute. The degree of cure α corresponding to each of these cure temperatures was determined in the manner described subsequently. The cure parameters are summarized in Table 1. Cooling took place at a rate of 3°C/min up to about 100°C. Below this temperature cooling was very slow (1°C/min).

Some of the Fiberite 976 resin specimens were also cured by temperature cycles shown in Figure 5. These cycles resulted in the same value of α ($\alpha = 0.87$) as the cure at 177°C for $1\frac{1}{4}$ hours. The resin specimens were cut from the cured plates. The dimensions of the specimens are given in Figure 2.

In addition to the pure resin specimens described above, specimens were also prepared containing a single fiber bundle. These specimens were fabricated by stretching the bundle along the length of the mold (Figure 1). Inside the mold the two ends of the bundle were tied with a wire to ensure that the cross-sectional area of the bundle remained nearly circular.

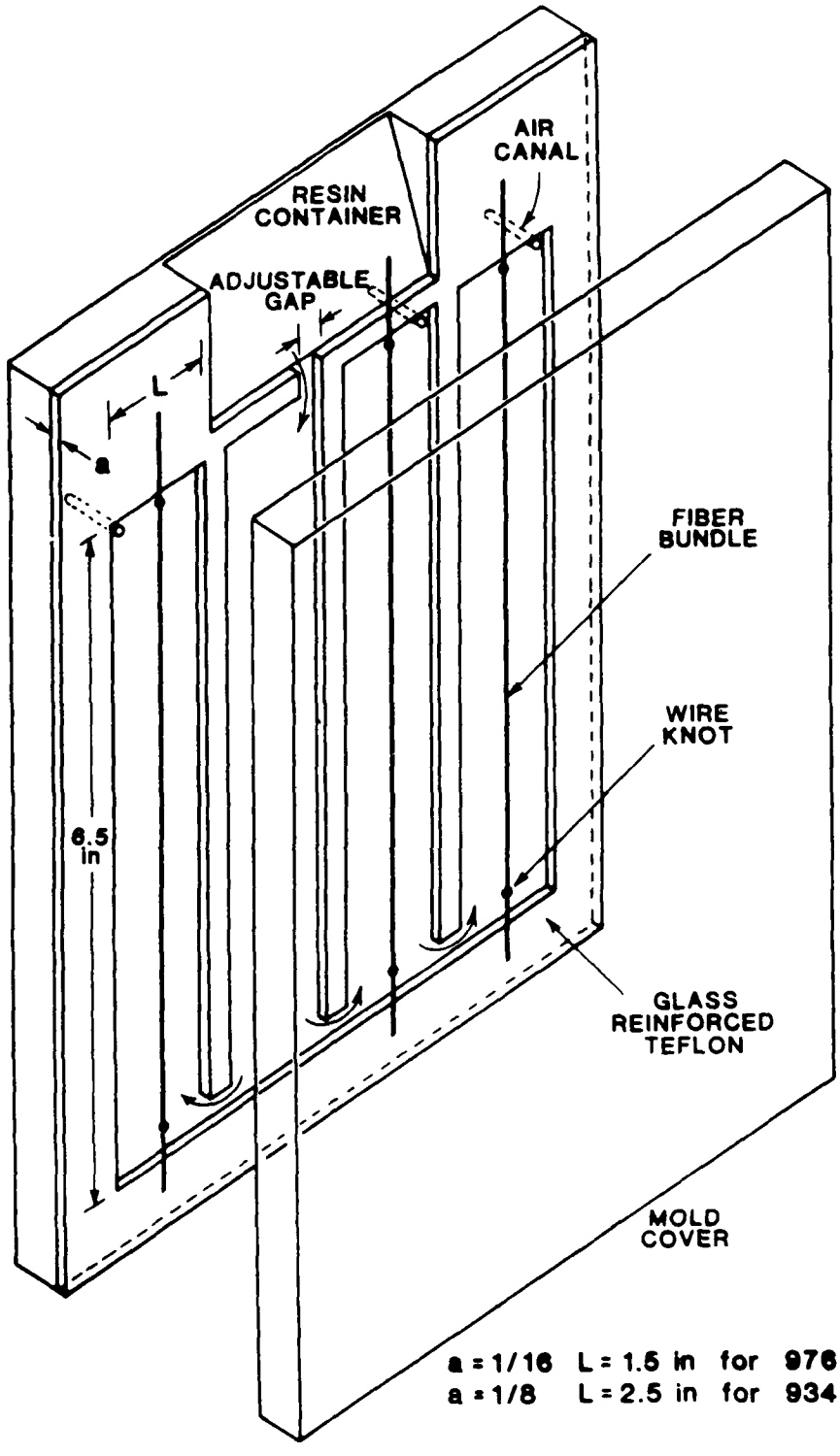
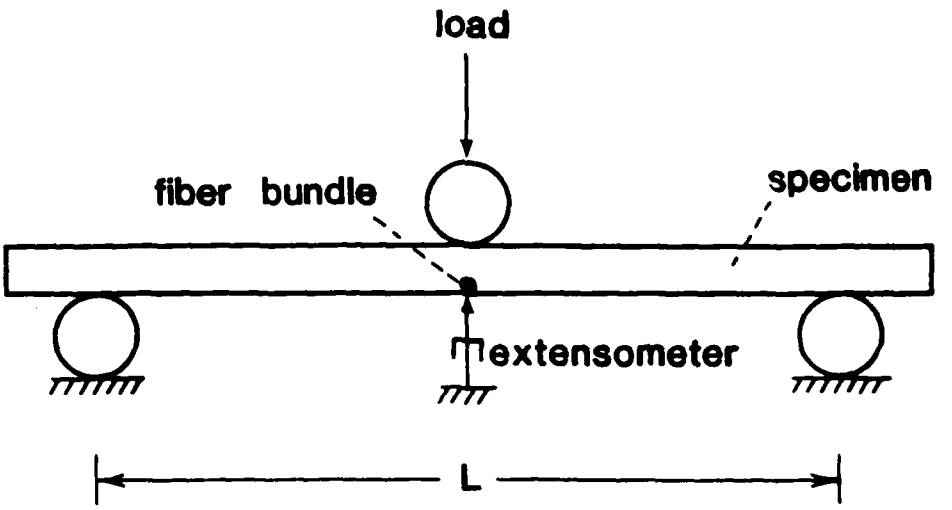


Figure 1. Schematic of the aluminum mold. (The cover is fastened to the mold by clamps.)

Table 1

Cure process parameters used in making the specimens. The initial heat-up rate to the final cure temperature was 3°C per minute.

	Cure Temp.	Cure Time	Degree of Cure (α)
Fiberite 976	100°C	35 h 15 min	0.54
	140°C	5 h 27 min	0.71
	177°C	1 h 15 min	0.87
	220°C	12 min	0.99
Fiberite 934	95°C	22 h 40 min	0.58
	130°C	4 h 31 min	0.75
	170°C	1 h 23 min	0.96
	210°C	25 min	0.99



	Fiberite 976	Fiberite 934
Span L	1.5	2.5
Thickness h	1/16	1/8
Width d	0.4	0.4

Diameter of load supports 1/8

All units in inches

Figure 2. Schematic of the three-point bend test and geometries of the test specimens.

Union Carbide "Thornel" T300 (3K) fiber bundles were used in the tests. Bundles with and without sizing were tested. Some of the fibers had a sizing provided by the manufacturer (UC 309, 0.5–1.6% of the fiber bundle weight). Fibers without sizing were also treated in our laboratory, providing a coating consisting of D.E.R. 332 (diglycidyl ether of bisphenol-A) supplied by Dow Chemical Company. The amounts of D.E.R. coatings applied were 1 or 2 percent of the fiber bundle weight.

The melted resin (prepared in the manner described above) was poured into the mold held vertically. The resin in the mold rose slowly. It required about 15 minutes for the resin to rise to the top of the 6.5-inch long fiber bundle. This slow rise enabled the resin to penetrate the fiber bundles and wet the fibers. The specimens were then cured according to the same schedule as the pure resin specimens (Table 1). The dimensions of the plates with fiber bundles were the same as those of the pure resin specimens (Figure 2).

After outgassing the Fiberite 934 resin for 1 hour, the viscosity proved to be too high to impregnate the fiber bundle. For this reason the bundles were preimpregnated in a solution of 70% Fiberite 934 and 30% solvent, which was provided by the manufacturer. After pre-impregnation the bundle was dried for five minutes at 95°C.

The specimens were cut to the proper size by a silicon carbide wheel using water as a coolant. After their manufacture (and at least two days before testing) the specimens were stored in a desiccator at room temperature.

Every specimen was subjected to a three-point bend test according to the relevant ASTM standard [8] (Figure 2). The load was applied using a constant deflection rate of 0.05 in per minute for the Fiberite 976 and 0.1 in per minute for the Fiberite 934 specimens. The load versus deflection and the deflection at failure were recorded. The deflection was measured by a gauge under the specimen in contact with it at the center of the support span and stationary relative to the specimen supports. The strain at failure at the outer surface of the specimen was calculated by the expression [8]

$$\epsilon_f = 6D_f h/L^2 \tag{1}$$

where D_f is the midspan deflection at failure, h the thickness and L the support span. The moduli (stiffnesses) of the specimens in bending E_b were also determined from the

load deflection curve, making use of the expression

$$E_b = L^3 \, m/4 \, A \, h^2 \tag{2}$$

where m is the slope of the curve and A is the cross-sectional area.

Photomicrographs were made of fiber bundles embedded in the matrix. These photomicrographs were used to inspect the cross-sectional areas of the bundles and to estimate the fiber volume fraction inside the bundle.

Differential scanning calorimetry (DSC) was performed on pure resin samples as well as on fiber sizing (UC309). For the latter tests the sizing was removed from the fiber bundles by immersing the bundles in the solvent Methyl Ethyl Ketone (MEK). The curing agent DDS was then added to the solution containing the sizing and MEK. The weight of the added DDS was 34 percent of the weight of the sizing removed from the fibers. (The weight of the sizing was determined by weighing the fiber bundle before and after the sizing was removed.) The MEK solvent was vaporized by blowing dry nitrogen over the solution. The remaining mixture of sizing and DDS was collected in a glass and used in the DSC measurements.

Section III

RESULTS

The fracture strains in bending of pure resin specimens and specimens containing a single fiber bundle were measured. Ten specimens were tested at each condition. In the figures presented in this section, the mean as well as the standard deviation in the data are indicated.

The data are presented in terms of both the maximum cure temperature and the degree of cure of the resin. The degree of cure corresponding to each cure temperature cycle was calculated by the expressions

$$\alpha = H_T/H_u \int_0^t (K_1 + K_2\beta^m)(1-\beta)^n \, dt \qquad \text{(for 976)} \qquad (3)$$

$$\begin{aligned} \alpha &= H_T/H_u \int_0^t (K_1 + K_2\beta)(1-\beta)(B-\beta)\, dt \qquad \beta \le 0.3 \\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(for 934)} \qquad (4) \\ \alpha &= H_T/H_u \int_0^t K_3(1-\beta)\, dt \qquad\qquad\qquad\qquad \beta > 0.3 \end{aligned}$$

where β is the temperature-independent isothermal degree of cure, H_T the heat generated during isothermal curing and H_U the ultimate heat measured during dynamic scanning of a resin sample. In case of Fiberite 976 $H_T/H_U = 0.0044\,T + 0.09$ for $T < 207°C$ and $H_T/H_U = 1$ for $T \ge 207°C$, whereas in case of Fiberite 934 $H_T/H_U = 0.00504\,T + 0.10$ for $T < 178°C$ and $H_T/H_U = 1$ for $T \ge 178°C$. The parameters K_1, K_2, and K_3 are defined as

$$\begin{aligned} K_1 &= A_1 \exp(-\Delta E_1/RT) \\ K_2 &= A_2 \exp(-\Delta E_2/RT) \qquad (5) \\ K_3 &= A_3 \exp(-\Delta E_3/RT). \end{aligned}$$

A_1, A_2, and A_3 are the pre-exponential factors, ΔE_1, ΔE_2, and ΔE_3 are the activation energies, R is the universal gas constant and T is the absolute temperature. B is a constant independent of the temperature. The values of these parameters are given in Table 2.

The expression for Fiberite 976 resin (Eq. 3), together with the corresponding constants, were taken from reference 9. The expressions for Fiberite 934 resin (Eq. 4) are the same as developed by Lee et al. [10] for Hercules 3501-6 resin. The constants to be used for Fiberite 934 resin were determined during the course of this investigation by performing differential scanning calorimetry in the manner described in reference 10.

Pure Resin

The fracture strains of Fiberite 976 and 934 resins are shown in Figure 3. For the 976 resin system the fracture strain increases monotonically, and reaches about 4.5 percent at maximum cure ($\alpha \simeq 0.99$). On the other hand, the fracture strain of the 934 resin system reaches a maximum of about 6.5 percent strain at $\alpha = 0.96$. The fracture strain then decreases significantly to about 3.5 percent at $\alpha = 0.99$.

For the Fiberite 976 resin system the load versus deflection curve was nearly linear. (A typical load versus deflection curve is shown in Figure 4.) Failure occurred in the elastic range, (i.e., where the load-deflection curve was nearly linear) for all degrees of cure. For the Fiberite 934 resin the load versus deflection curve became nonlinear at higher loads, as illustrated in Figure 4. At degrees of cure less than about 0.8 as well as at the highest degree of cure ($\alpha \simeq 0.99$), failure occurred in the elastic range. However, at the intermediate degree of cure ($\alpha \simeq 0.9$) failure occurred beyond the "yield point," in the inelastic (nonlinear) range of the load-deflection curve. This suggests that the resin's stress-strain behavior changes as the cure progresses.

The stiffness (moduli) in bending E_b of Fiberite 976 and 934 resins are shown in Figure 3. Each data point shown is the average of four tests. In addition the maximum and minimum values of the stiffnesses are indicated. The data follow the expected trend. Namely, the fracture strain increases with decreasing stiffness and decreases with increasing stiffness.

The results in Figure 3 point out the significant fact that an increase in degree of cure does not always ensure an increase in mechanical properties.

Table 2

The values of the constants used in calculating the degree of cure (Equations 3–5).

		Fiberite 976	Fiberite 934
A_1	(min^{-1})	2.64×10^5	2.45×10^{11}
A_2	(min^{-1})	4.23×10^5	-6.75×10^{12}
A_3	(min^{-1})	--	4.08×10^3
ΔE_1	(J/mol.)	6.25×10^4	9.63×10^4
ΔE_2	(J/mol.)	5.68×10^4	1.06×10^5
ΔE_3	(J/mol.)	--	4.19×10^4
m		1.03	--
n		1.22	--
B		--	0.537

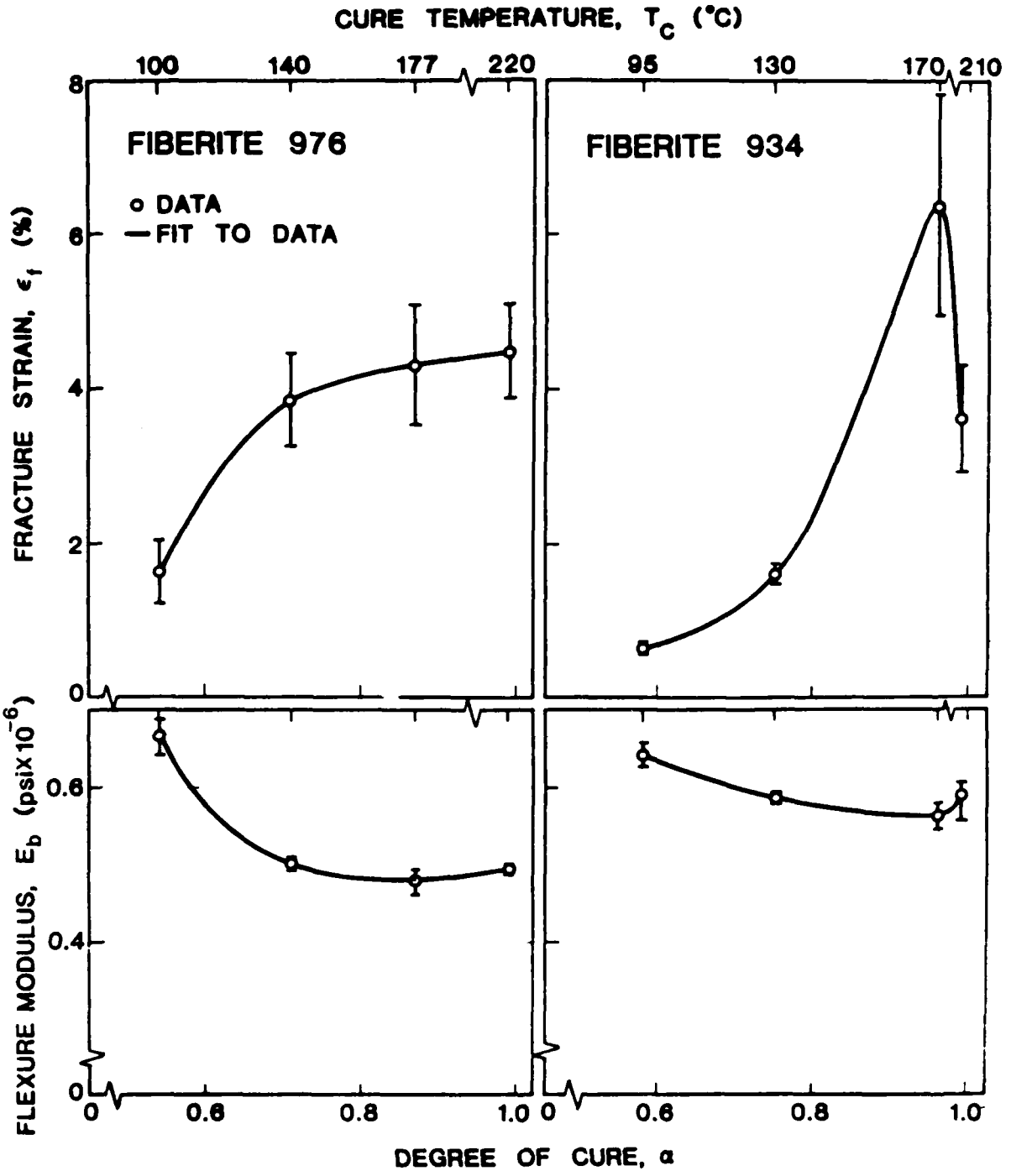


Figure 9. Fracture strains and moduli in three-point bending of Fiberite 976 and 934 resins cured at different temperatures. Cure cycles given in Table 1. Bars represent standard deviations about the mean in case of fracture strain and scatter in the data in case of the moduli.

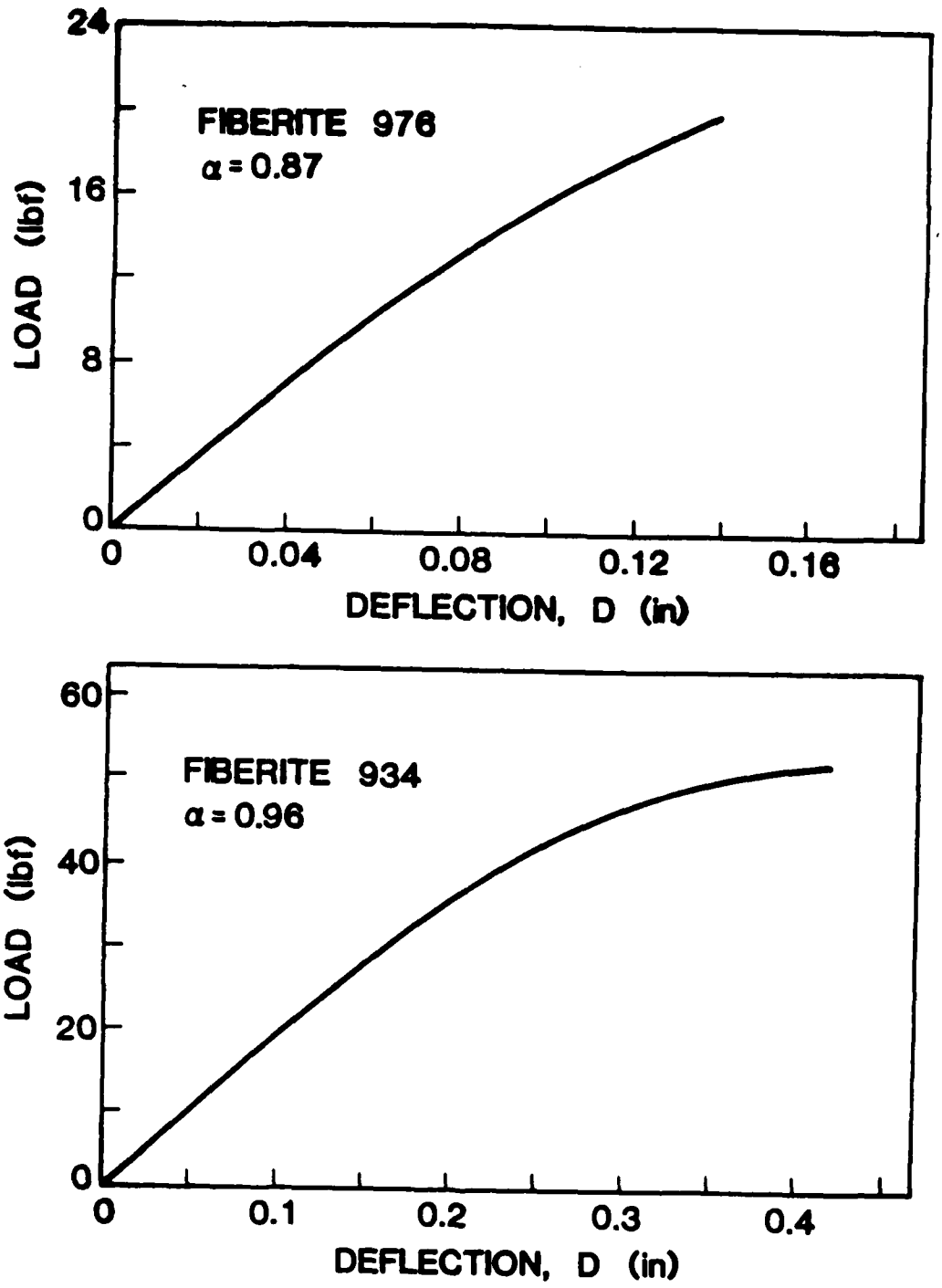


Figure 4. Typical load versus deflection curves for pure resin specimens subjected to three-point bending. Specimens were cured to the indicated degree of cure (α) values.

One additional observation is worth noting. The same degree of cure can be achieved by different cure cycles, as illustrated in Figure 5. In this study, for Fiberite 976 resin specimens a degree of cure $\alpha = 0.87$ was achieved by three different cure cycles. Although the degree of cure was the same, the fracture strains and bending stiffnesses differed somewhat for specimens cured by different cure cycles (Figure 5). It appears that in addition to the value of α, the route by which a given α is reached also influences the mechanical properties.

Fiber Bundle Bond Strength

The fracture strains of specimens containing fiber bundles are presented in Figures 6 and 7. For all the specimens represented in these figures failure occurred in the fiber bundle. Hence, these data are indicative of the strength of the fiber-matrix interface inside the bundle. This is especially true when the fracture strain at one particular degree of cure (cure temperature) is considered. A change in fracture strain due to the use of fibers with a different sizing, or different amounts of sizing, can only be caused by the sizing and not by the matrix.

Fracture strains of specimens containing unsized (uncoated) and sized (coated with sizing UC 309 provided by manufacturer) fiber bundles are compared in Figure 6. The fracture strains of specimens containing either uncoated (no sizing) or coated (with sizing) fiber bundles are considerably lower than the fracture strain of the pure resin. These test results were analyzed statistically to determine whether the increase of the bond strength due to sizing is significant. This was done by assuming the data to be of normal distributions with unequal unknown variances. The hypothesis that the mean fracture strain remains unchanged due to the sizing was tested against the hypothesis that the sizing improves the mean fracture strain making use of a random variable distributed as Student's t [11]. A test on the 1% significance level rejected the hypothesis that the fracture strain for specimens with sized as well as with unsized fibers is the same for materials with $\alpha = 0.54$ and $\alpha = 0.99$. Thus in these cases the increase in fracture strain due to the sizing is significant.

A clearer indication of the effects of sizing is obtained from the data generated with specimens containing fiber bundles coated with 1 or 2 percent (by fiber weight) of D.E.R. 332. The fracture strains of specimens containing fibers coated with 1 and 2 percent D.E.R.

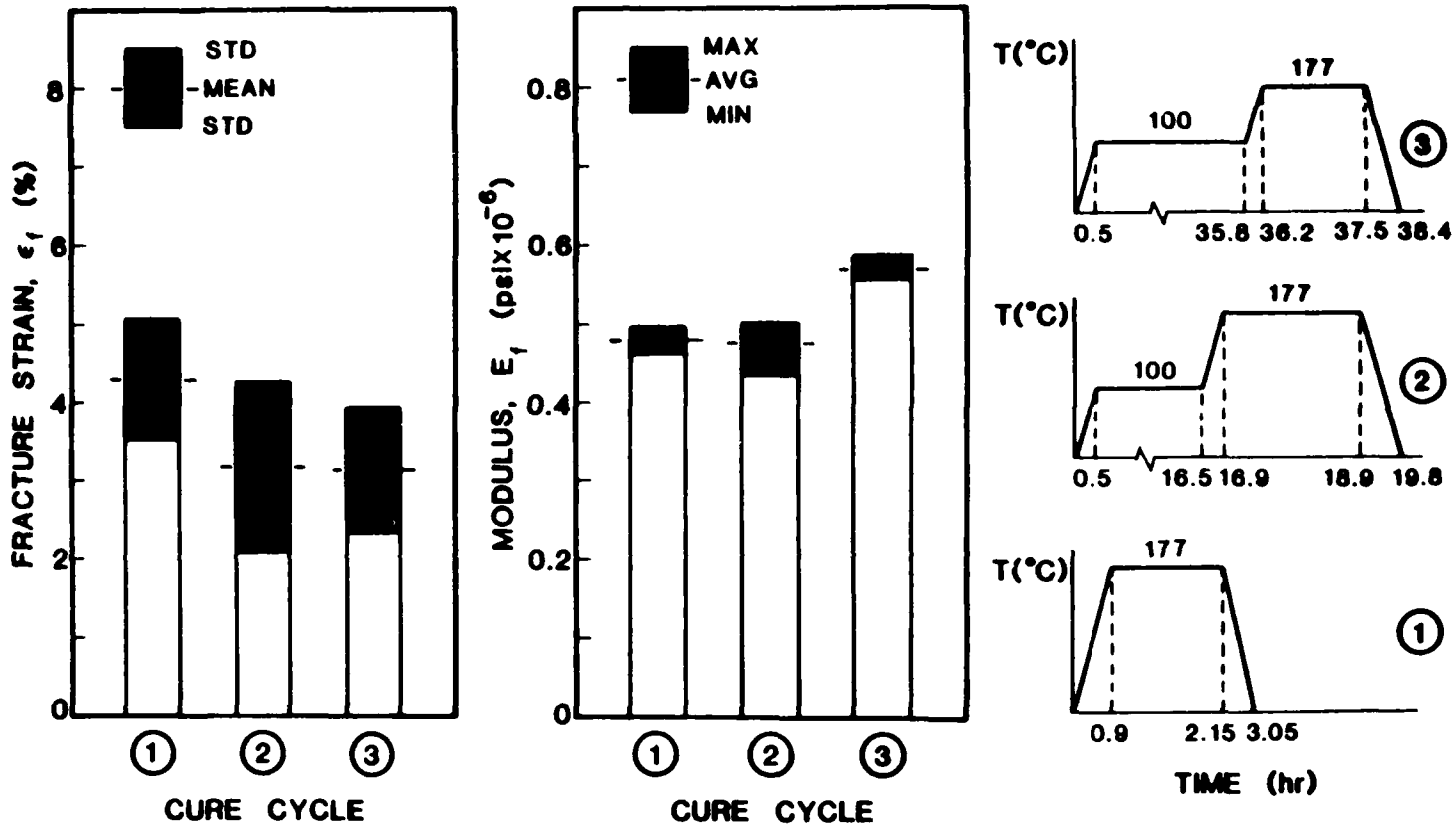


Figure 5. The fracture strains and moduli in three-point bending of Fiberite 976 resin specimens cured by three different temperature cycles to the same value of $\alpha = 0.87$.

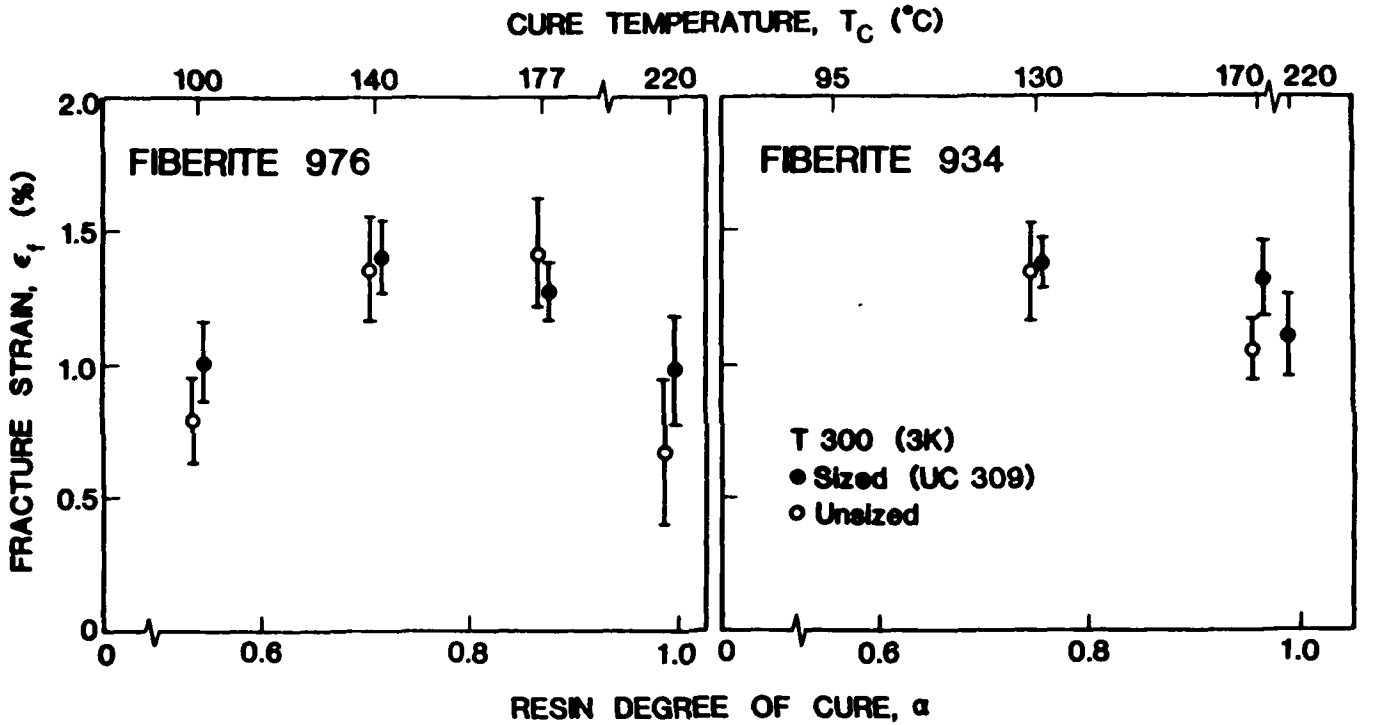


Figure 6. The fracture strains in three-point bending of specimens containing a single T300 (3K) fiber bundle embedded in Fiberite 976 or 934 resin specimens. The fibers were either uncoated (no sizing) or coated with sizing provided by the manufacturer (Union Carbide 309). Adjacent data points are for the same degree of cure. The points were separated slightly to show the bars representing the standard deviation around the mean.

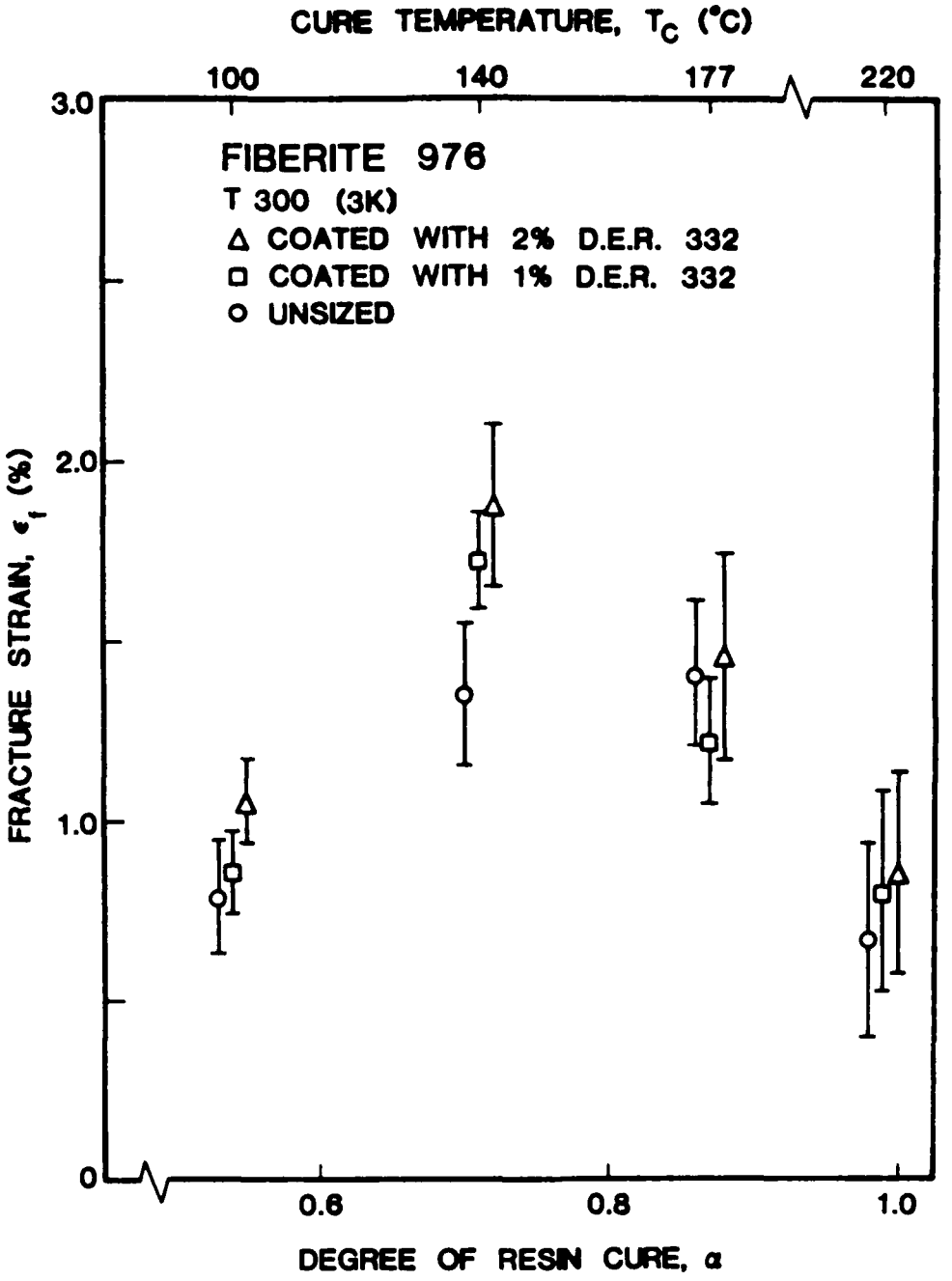


Figure 7. The fracture strains in three-point bending of specimens containing a single T300 (3K) fiber bundle embedded in Fiberite 976 resin specimen. The fibers were either uncoated (no sizing) or coated with sizing consisting of either 1% or 2% of D.E.R. 332. Adjacent data points are for the same degree of cure. The points were separated slightly to show the bars representing the standard deviation around the mean.

332 differed, the larger amount of coating generally resulting in higher fracture strains (Figure 7). This result was also analyzed statistically, using the procedure mentioned above. The statistical analysis leads to the conclusion that the increase in fracture strain is significant for the material with 2% D.E.R. 332 sizing cured at $\alpha = 0.54$, 0.71, and 0.87. These data were tested against the fracture strain of the unsized material at a significance level of 1%, with exception of the material cured up to $\alpha = 0.87$ which was tested against the material with 1% D.E.R. 332 sizing at a significance level of 5%. The material with fiber bundles with 1% D.E.R. 332 in comparison with the unsized material, however, only shows a significant increase of the bond strength at $\alpha = 0.71$.

In interpreting the aforementioned data (Figures 6 and 7) it is important to bear in mind that sizing affects the fracture strain in two different ways. First, sizing affects the strength of the bond at the fiber-matrix interfaces. Second, the sizing affects the fiber density within the fiber bundle for the following reason. Sizing promotes the wetting of the fiber surface by the resin. This wetting introduces capillary forces which tend to pull the individual fibers together, thereby decreasing the fiber bundle cross section and increasing the fiber density. This is illustrated by the photomicrographs in Figure 8.

For Fiberite 976 resins the fiber density (defined as the fiber area divided by the bundle cross-sectional area) ranged from 0.39 for uncoated fibers to 0.52 for fibers coated with sizing. For Fiberite 934 resins the fiber density was approximately 0.41 for fibers with and without sizing. In this case there is no influence of the sizing on the fiber bundle cross section because of the preimpregnation process applied before embedding the bundle.

The measured fracture strain is influenced by both of the aforementioned effects of the sizing, i.e., by changes in both fiber-matrix bond strength and in fiber bundle geometry. The relative magnitudes of these two effects cannot be deduced from the data. Nevertheless, the following important observation can be made. Sizing increases the fiber density (see Figure 8) which, in turn, results in a decrease in the strength (due to an increase in stress concentration introduced by the proximity of the fibers). Thus, due to this effect of the sizing on the fiber density, the fracture strain is reduced. However, the data in Figures 7 and 8 show the opposite effect, namely an increase in fracture strain. Apparently, the decrease in strength due to the increase in fiber density was compensated by an increase in the bond strength.

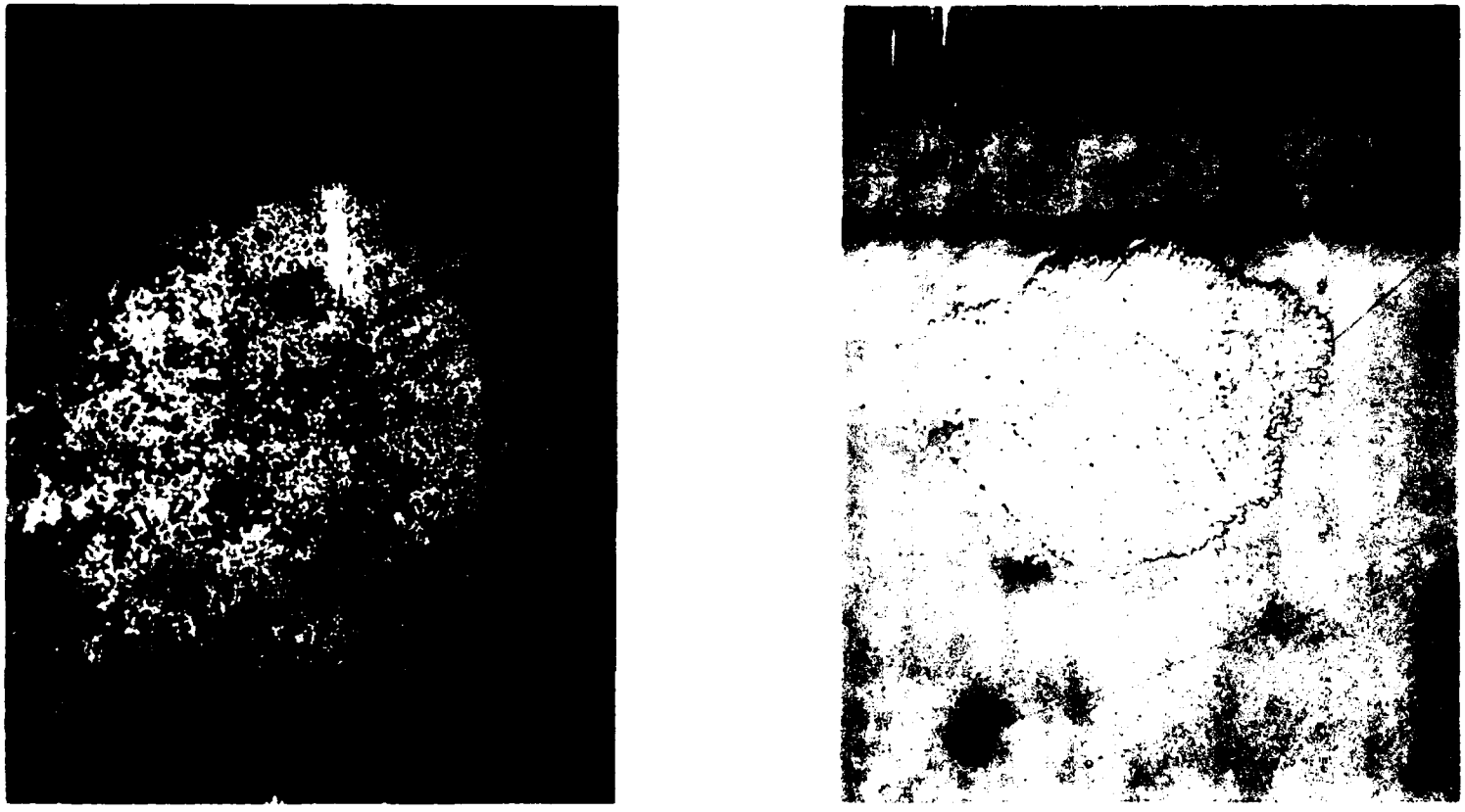


Figure 8. Typical photomicrographs with the same magnification of Thornel T300 (3K) fiber bundles embedded in Fiberite 976 resin. *Left*: fibers uncoated (no sizing). *Right*: fibers coated with sizing provided by the manufacturer (Union Carbide 309).

The cure temperature seems to have a slight effect on the fracture strain. As the cure temperature (and resin degree of cure) increases the bundle fracture strain seems to decrease, at least above cure temperatures of 130°–140°C (corresponding resin degree of cure $\alpha = 0.72$ for 976, and $\alpha = 0.76$ for 934). For Fiberite 976 resin at the lower cure temperature of 100°C (corresponding $\alpha = 0.54$) the fracture strain is lower than at higher temperatures. With Fiberite 934 resin, data at temperatures below 130°C could not be generated because the specimens were too brittle and broke in the mold. The data in Figure 7 suggest that the fracture strain increases slightly with cure temperature (and with corresponding resin degree of cure) up to a maximum, and then decreases with cure temperature (and resin degree of cure).

The maximum fracture strains of specimens containing a fiber bundle was reached at a different cure temperature (and resin degree of cure) than the maximum pure resin fracture strain. This is illustrated in Figure 9 where the fracture strains of pure resin specimens and specimens with fiber bundles are presented.

Based on these fracture data the following qualative comparison of the matrix and bond strength can be made. If the bond strength is as high as the matrix strength the fracture strain of the specimens with a fiber bundle is close to the fracture strain of the matrix alone. However, due to stress concentrations caused by the fibers, the fracture strain of specimens with embedded fibers will always be smaller. The smallest difference in fracture strain between pure resin and resin with fiber bundle occurs for Fiberite 934 resin at a degree of cure of $\alpha = 0.75$. In this case the bond strength is close to the matrix strength as can be concluded from the fact that some specimens with an embedded bundle broke outside the bundle area. (The fracture strains of these tests are not used for the determination of the mean fracture strain as mentioned before.) Under-curing of the Fiberite 976 resin ($\alpha = 0.54$ at $T_c = 100$°C) also leads to a bond strength close to the matrix strength. An improvement of the matrix due to curing up to higher degrees of cure ($\alpha = 0.96$ for Fiberite 934 and $\alpha \geq 0.71$ for Fiberite 976) only improves the bond strength on a much smaller scale (Fiberite 976) or not at all (Fiberite 934), as can be concluded from the fracture strain of specimens with embedded fibers.

That the resin and the sizing cure at different rates is further borne out by the results of the dynamic differential scanning calorimetry (Figure 10). The total amount of heat

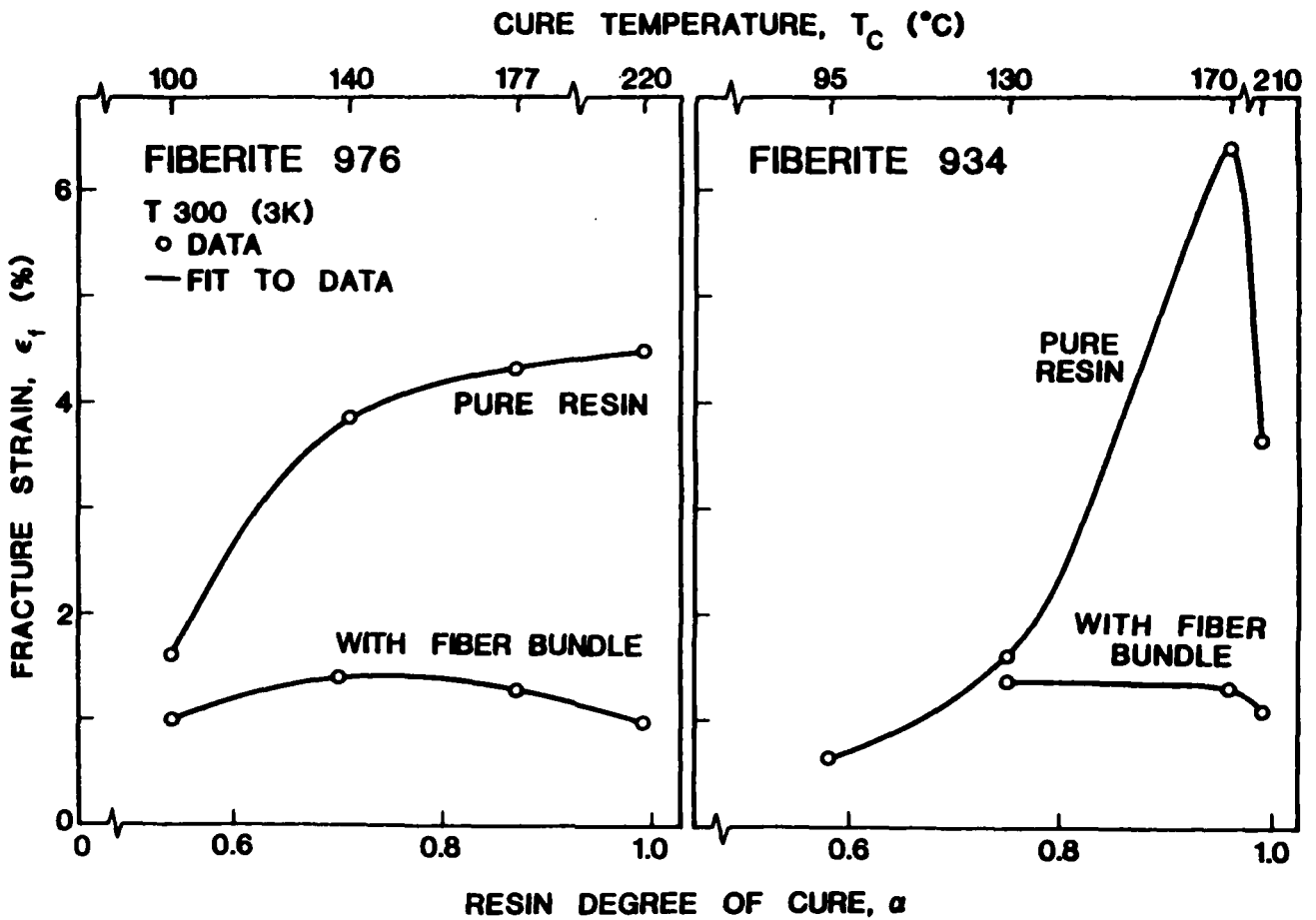


Figure 9. Comparison between the fracture strains in three-point bending of pure Fiberite 976 and 934 resin specimens and specimens containing T300 fiber bundles coated with sizing provided by manufacturer (Union Carbide 309).

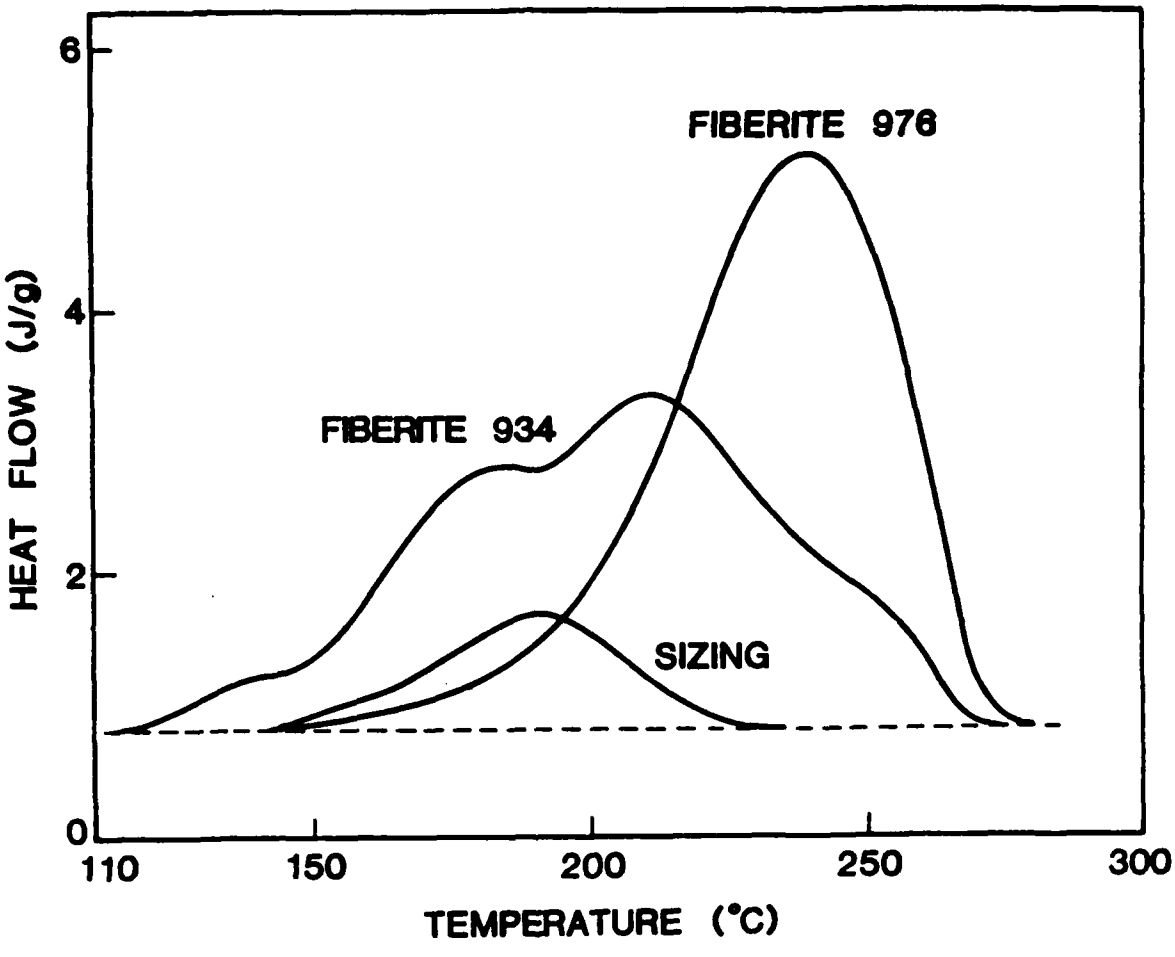


Figure 10. The result of differential scanning calorimetry performed on Fiberite 976 and 934 resins and on fiber sizing containing 34% DDS by weight. Dynamic scanning at the rate of 10°C/min.

released by the sizing is considerably less than the heat released by the resins. Also, curing of the sizing is completed before curing of the resin.

The results in Figure 9 show that a composite cured for maximum resin properties may not have the maximum fiber bond strength and, conversely, a composite cured for maximum fiber bond strength may not have the maximum resin strength.

Section IV

CONCLUSIONS

The following major conclusions can be drawn on the basis of the data generated in this study.

(1) The cure temperature and, correspondingly, the degree of cure affects the mechanical properties of resins. However, an increase in the degree in cure does not necessarily imply an increase in mechanical properties. In fact, the mechanical properties may decrease with an increase in the degree of cure.

(2) The fracture strains of specimens containing a fiber bundle (and loaded perpendicular to the fibers) is lower than the fracture strains of pure resins. The difference is rather small when the bond strength approaches the matrix strength, whereas the difference is larger when the bond strength is smaller than the matrix strength.

(3) The fiber bundle-resin bond strength (as manifested by the fracture strain) is affected by the cure temperature cycle. The maximum bond strength is established at a different cure cycle than the maximum resin strength.

(4) Sizing appears to increase the fracture strain of specimens containing a fiber bundle.

(5) Sizing affects the fracture strain of specimens containing fiber bundles in two ways. On the one hand, sizing increases the fiber density inside the bundle, thereby reducing the fracture strain. On the other hand, sizing increases the bond strength between the fibers and the matrix, thereby increasing the fracture strain. The measured fracture strain is due to a combination of these two effects.

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